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ELECTRICAL AND THERMOMECHANICAL PROPERTIES OF EPOXY FILLED HYBRID COVALENT TREATED MWCNTS/GNPS NANOCOMPOSITES

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ABSTRACT

The investigations on electrical, mechanical and thermal properties of epoxy filled hybrid treated Multi-Walled Carbon Nanotubes (MWCNTs) and Graphene Nanoplatelets (GNPs) were reported in this research. DGEBA epoxy and hybrid MWCNTs/GNPs were respectively used as a matrix and nanofiller in developing improvement into the epoxy polymer. The properties and performances of epoxy hybrid treated MWCNTs/GNPs nanocomposites were investigated and evaluated in this works. The MWCNTs which have an inert surface characteristic are tend to agglomerate and need to be modified in lowering their viscosity of epoxy due to good dispersion of MWCNTs fillers within the matrices. Amino Propyl Triethoxy Silane (APTS) chemical was used as a medium for covalent functionalization utilizing a simplified treatment approaches. Surface treatment evaluation was done by performing a Fourier Transform Infrared Spectroscopy (FTIR) and Raman spectroscopy to further confirm the success of the covalent functionalization performed to the MWCNTs surfaces. Then, the GNPs at various filler loadings were added into the MWCNTs and become hybrid MWCNTs/GNPs. The nanocomposites samples with 0.00 wt.%, 0.25 wt.%, 0.50 wt.%, 0.75 wt% and 1.00 wt.% of GNPs loadings were tested by using various electrical, mechanical and thermal testing which are surface resistivity, permittivity, tensile test, flexural test, and DSC analysis. For electrical testing, surface resistivity shows the highest resistivity for epoxy/MWCNTs without GNPs filler while permittivity shows increment for highest GNPs filler loading. In term of mechanical testing, tensile and flexural testing result shows the improvement for epoxy hybrid MWCNTs/GNPs with 30.04% and 38.33% increament compared to the epoxy/MWCNTs without GNPs filler. The experimental results shows that the electrical, mechanical and thermal properties were significantly investigated by the covalent treatment onto the MWCNTs surfaces and addition of GNPs filler. Scanning electron microscopy (SEM) observations on the fractured surfaces shows that the properties improvement in the nanocomposites and filler dispersion as well as the matrix-filler interaction is directly interrelated with the success of covalent functionalization of MWCNTs and GNPs filler addition.

ABSTRAK

Siasatan keatas ciri-ciri elektrikal, mekanikal dan haba epoksi yang diisi campuran Multi-Walled Carbon Nanotube (MWCNTs) yang dirawat dan Graphene Nanoplatelets (GNPs) nanokomposit dilaporkan dalam kajian ini. Epoksi DGEBA dan campuran pengisi MWCNTs/GNPs telah digunakan sebagai matriks dan tetulang sebagai peningkatan kepada polimer epoksi. Ciri-ciri dan prestasi epoxy yang diisi campuran MWCNTs/GNPs disiasat dan dinilai dalam kerja-kerja ini. MWCNTs yang mempunyai ciri-ciri permukaan lengai yang cenderung untuk menggumpal perlu diubah suai untuk menurunkan kelikatan epoksi disebabkan penyebaran yang baik oleh pengisi MWCNTs di dalam matriks. Kimia Amino Propyl Triethoxy Silane (APTS) telah digunakan sebagai medium untuk rawatan kovalen kerana ia adalah satu pendekatan rawatan yang mudah. Penilaian rawatan permukaan seperti Analisis Fourier Infra Merah (FTIR) dan spektroskopi Raman telah dilakukan untuk mengesahkan lagi kejayaan rawatan kovalen yang telah dilakukan keatas permukaan MWCNTs. Selepas itu, GNPs yang mempunyai berat yang berlainan dimasukkan kedalam MWCNTs lalu menjadi campuran MWCNTs/GNPs. Sampel nanokomposit yang mempunyai berat GNPs yang berlainan iaitu 0.00 wt.%, 0.25 wt.%, 0.50 wt.%, 0.75 wt.% dan 1.00 wt.% telah diuji dengan menggunakan pelbagai ujian elektrikal, mekanikal dan haba iaitu ujian ketahanan permukaan, ujian ketelusan, ujian tegangan, ujian lenturan dan analisis DSC. Untuk ujian elektrikal, ujian ketahanan permukaan menunjukkan ketahanan yang tinggi bagi epoksi/MWCNTs tanpa pengisi GNPs sementara ujian ketelusan menunjukkan peningkatan bagi pengisi GNPs yang paling tinggi. Dari segi ujian mekanikal, hasil ujian tegangan dan ujian lenturan menunjukkan peningkatan untuk epoksi yang diisi campuran MWCNTs/GNPs dengan peningkatan sebanyak 30.04% dan 38.33% berbanding epoksi/MWCNTs tanpa pengisi GNPs. Keputusan eksperimen menunjukkan bahawa ciri-ciri elektrikal, mekanikal dan haba diselidik dengan ketara hasil daripada rawatan kovalen yang dilakukan ke atas permukaan MWCNTs dan pertambahan pengisi GNPs. Pemerhatian yang dijalankan melalui Pengimbas Mikroskopi Elektron (SEM) terhadap permukaan patah menunjukkan bahawa adanya peningkatan kepada ciri-ciri nanokomposit dan penyebaran oleh pengisi serta interaksi antara matriks dan pengisi adalah saling berkaitan disebabkan oleh kejayaan rawatan kovalen keatas MWCNTs dan pertambahan pengisi GNPs.

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LIST OF ABBREVIATIONS, SYMBOLS AND NOMENCLATURE

APTS	-	Amino-Propyl Triethoxy Silane
ASTM	-	American Society for Testing and Materials
CNT	-	Carbon Nanotubes
CVD	-	Chemical Vapor Deposition
DGEBA	-	Diglycidyl Ether of Bisphenol A
DGEBF	-	Diglycidyl Ether of Bisphenol F
DSC	-	Differential Scanning Calorimetry
DWCNT	-	Double Walled Carbon Nanotube
FESEM	-	Field-Emission Scanning Electron Microscopy
FTIR	-	Fourier Transform Infrared Spectroscopy
HiPco	-	High-Pressure Carbon Monoxide
HCl	-	Hydrochloric acid
HMPA	-	Hexydro-4-methylphthalic anhydride
Hz	-	Hertz
MEKP	-	Methyl Ethyl Ketone Peroxide
MWCNT	-	Multi Walled Carbon Nanotubes
PMC	-	Polymer Matrix Composite

SEM	-	Scanning Electron Microscope
SiC	-	Silicon Carbide
SOP	-	Standard Operating Procedure
SWCNT	-	Single Walled Carbon Nanotubes
TEM	-	Transmission Electron Microscopy
TGMDA	-	Tetraglycidyl Methylene Diamiline
TGPAP	-	Triglycidyl P-Amino-Phenol
TiO_2	-	Titanium Oxide
wt%	-	Weight percentage
ZrO_2	-	Zirconium dioxide
°C	-	Degree Celsius
kN	-	Kilo Newton
mm	-	Milimeter
nm	-	Nanometer
rpm	-	Revolutions per minute
µm	-	Micrometer
π	-	Pi

CHAPTER 1

INTRODUCTION

1.1 Background of study

Polymer matrix composite (PMC) has been described as the combination of polymer and reinforcement filler. There are various type of polymer materials related to PMC including epoxy as a base matrix. PMC has been choosen as the material because it is cheap and easy to use compared than ceramic matrix composite (CMC) and metal matrix composite (MMC). Epoxy resin is a generic name for compounds that have two or more oxirane rings which are epoxy groups in one molecule, and are cured three-dimensionally by addition of suitable curing agent. The usage of epoxy was expanded in early 1946 and are commonly used in industries afterwards. Nowadays, epoxy resins are commonly used in wide range of applications such as the fabrication of fiberglass based composite industries, similar as polyester resin. However, epoxy resin has their limitation and drawbacks in terms of their brittleness that are not suitable for some importants applications, especially for high performance engineering purposes.

The purpose of this research is to investigate the electrical and thermomechanical properties of epoxy filled hybrid MWCNTs/GNPs nanofiller, through covalent surface modification strategy of multi-walled carbon nanotubes (MWCNTs) filler. In this research, diglycidyl ether of bisphenol A (DGEBA) epoxy was used as a matrix. The DGEBA epoxy was chosen than diglycidyl ether of bisphenol F (DGEBF) epoxy because of their widely used applications especially in the polymer field. DGEBA epoxy has a molecular mass of 340.42 $g.mol^{-1}$ and density of 1.16 g/ml at 25ºC. The price of DGEBA epoxy is $65 for 25g, while DGEBF epoxy has a molecular mass of 312.36 and price of $125 for 1g. Both DGEBA and DGEBF must be stored in the refrigerator or under an inert environment to maintain their condition and properties of epoxy resin. According to the characteristics comparison between the DGEBA and DGEBF, it was shown that the DGEBA epoxy are cheaper and easy to handle than DGEBF.

Due to advance in industrial research nowadays, many improvements have been made to the epoxy resin characteristic. As mentioned above, this research is conducted to investigate the electrical, mechanical and thermal properties of produced epoxy nanocomposites. Through this research, the polymer nanocomposites will be change form non-conductive material to conductive material for electrical application. Hence, one way to improve the electrical and thermomechanical performance of epoxy, is through adding the conductive nanofiller and performing the surface modification to the selected nanofiller. Particularly, the utilization of micro- and nanofiller could offer new approaches towards improving the conductivity systems that operated at higher temperatures and electrical stress (Ilona *et al*., 2016). For example, carbon nanotubes (CNTs) and graphene nanoplatelets (GNPs) are the most popularly explored nanomaterials, since both of these carbon nanomaterials derivatives were offering abundant promising and outstanding benefits towards improving the epoxy resin matrix end performances. By adding carbon nanofiller such as CNTs and GNPs into the epoxy resin, it will give good advantages towards the resulted nanocomposites that exhibiting improved electrical, mechanical and thermal properties relative to those of the neat polymer matrix (Chang *et al*., 2015).

According to Li *et al*. (2013), the electrical and mechanical properties polymer nanocomposites can be improved by adding of CNTs owing to their high elastic modulus as well as excellent thermal and electrical conductivity. Meanwhile, GNPs becoming more attractive since it can produce an impressive enhancement in the resulted composites properties even at a very low filler content addition. Besides, GNPs sheet is considered to be a kind of good thermal conductive filler or additive for thermal engineering application, since their layered structure are able to form an effective pathway for heat transfer (Song *et al*., 2013). GNPs also become a very promising filler for polymers composites application since it has large specific surface area, higher aspect ratio, and extraordinary electrical and thermal conductivities characteristics (Zhang *et al*., 2012).

Carbon nanotubes were divided into three major types which are single-walled carbon nanotubes (SWCNTs), double-walled carbon nanotubes (DWCNTs) and multi-walled carbon nanotubes (MWCNTs). The MWCNTs was used in this research as reinforcement materials because of several factors whereby the bulk synthesis is easy and the chance of defect formation appear is less. In this research, the MWCNTs were treated by covalent treatment and subsequently added with GNPs before being mixed with the epoxy resin in order to observe their viscosity, dispersion and interaction between the epoxy, carbon nanotubes and GNPs. Later, the electrical, mechanical and thermal properties of epoxy nanocomposites were observed by conducting appropriate testing and surface morphological observation via Scanning Electron Microscopy (SEM). This study is crucially important to explore the potential of hybrid MWCNTs surface modification with GNPs addition towards the enhancement of electrical and thermomechanical behavior of epoxy based nanocomposites especially for electrical application.

1.2 Problem statement

Up till now, the study on mechanism of interaction between the epoxy matrix, MWCNTs and GNPs in the complex hybrid nanocomposites systems is still scarce. Thus, this research provides a kick start to explore related interaction phenomenon between the matrix-hybrid nanofiller, as to understand the electrical and thermomechanical properties of epoxy nanocomposites and the fundamental knowledge about the nanofiller reinforcement in epoxy thermoset nanocomposites system. In order to investigate the electrical, mechanical and thermal properties of epoxy based hybrid nanocomposites, there are several possible addition and modification need to be done into the nanofiller system. However, the incorporation of hybrid MWCNTs/GNPs nanofiller into the epoxy matrix resin are not as easy as just mixing it. There are several difficulty may arise during the effort of combining epoxy resin with hybrid MWCNTs/GNPs nanofiller. One of them is the viscosity rise-up issue for epoxy resin. The viscosity of the epoxy resin may increase due to the agglomeration of MWCNTs and GNPs. The untreated MWCNTs were easily to form agglomeration because of their high surface area characteristic and dimensional factors.

Besides, MWCNTs and GNPs are easy to entangle due to complex dimensional effect and high aspect ratio. The higher content addition of MWCNTs and GNPs also can cause high viscosity condition of MWCNTs/GNPs epoxy uncured resin mixture that may further worsen the dispersion of filler in the epoxy matrix. As a consequence the epoxy resin was not able to fully interacted into the surface of MWCNTs and GNPs. The phenomenon of bad dispersion also can cause defects formation in epoxy composites after cured. Besides, worse dispersion condition of MWCNTs and GNPs in the polymer matrix is due to the van der waals interaction among carbon nanotubes and GNPs which further caused agglomeration and bundles formation between the tubes and platelets. After that, it is about interaction between matrix and reinforcement filler. The epoxy resin as matrix phase does not have good interaction with the MWCNTs and GNPs surface. This is because the untreated surface of MWCNTs has low ability to interact with the epoxy solution due to lack of functional group to promote the matrix-filler interaction. Hence, functionalization into MWCNTs filler are required, specifically to improve the dispersion and interfacial interaction between the MWCNTs/GNPs with epoxy resin.

To improve interface interaction between MWCNTs/GNPs with epoxy resin, a procedure known as surface modification by chemical functionalization that, also known as covalent treatment was often utilized. Amino-functionalized carbon nanotubes exhibit higher surface energy and have much better wettability with epoxy resin. Therefore, the covalent treatments have been conducted only towards the MWCNTs surface in order to solve the above-mentioned problems because this research is the improvement from the previous research. Then, through this research, treated MWCNTs and untreated GNPs will be used as nanofiller in order to improve the properties of produced nanocomposites.

1.3 Objectives

The main objectives of this research are:

1. To synthesize the epoxy filled with hybrid treated MWCNTs/GNPs nanofiller via solution casting method.
2. To investigate the effects of epoxy filled with hybrid treated MWCNTs/GNPs nanofiller at different hybrid ratio towards the improvement of electrical and thermomechanical properties of resulted nanocomposites.
3. To evaluate the matrix-filler interaction mechanism for epoxy filled with hybrid treated MWCNTs/GNPs based on the fracture-surface morphological observation via Scanning Electron Microscope (SEM).

1.4 Scope of study

In this research, epoxy resin was used as a matrix and hybrid MWCNTs/GNPs as a reinforcement. The DGEBA epoxy with hardener and hybrid MWCNTs/GNPs nanofiller with 0.50 wt.% MWCNTs and 0, 0.25 wt.%, 0.50 wt.%, 0.75 wt.%, and 1.00 wt.% GNPs were used as matrix and reinforcement in this research study respectively. The epoxy filled hybrid MWCNTs/GNPs will be prepared via solution casting method. Solution casting method was chosen than the other method because total manufacturing cost for both production volumes and prototype that are comparatively low than the conventional method. Then, the MWCNTs were treated by covalent functionalization in order to enhance their interaction between GNPs and epoxy matrix.

Apart from that, the electrical properties of epoxy nanocomposites were tested by surface resistivity test and permittivity test while mechanical properties were tested by using the tensile test and flexural test. The tensile test was performed by applying a force using uniaxial load to measure the applied load and the elongation of the samples while flexural test was executed to examine and evaluate the stiffness behavior and the ability to resist deformation under the load applied. For tensile test, the fractured specimen was cut and mounted before performing the surface morphological observation by SEM. The mounted sample was first gold coated to eliminate or reduce the charging effects during the observation that may obstruct clear evaluation for the establishment of interaction mechanism between epoxy matrix and their hybrid MWCNTs/GNPs nanofiller system.

The FTIR and Raman Spectroscopy were used to analyze the chemical and structural interaction between the matrix and filler as well as to further confirmed the success of covalent surface modification that are performed to the MWCNTs. The thermal properties evaluation was performed by using the differential scanning calorimetry (DSC) to analyze the thermal characteristic of produced hybrid nanocomposites. Towards the end, the efficiency of surface modification on MWCNTs and hybrid MWCNTs/GNPs that affecting the end results performance of the nanocomposites will be thoroughly evaluated by comparing each performance tested that involving the electrical, mechanical and thermal attributes.

1.5 Thesis organization

This research is organized into several sub-topic and chapters. The introduction had begun as Chapter One that provides the background of the research, problem statement, objectives, thesis scope and also thesis organization. Chapter Two briefly discussed about the literature review of the research including related theories and investigations of the epoxy, carbon nanotubes, graphene nanoplatelets, electrical properties and thermomechanical properties by the previous researcher. All these information are important to understand the electrical and thermomechanical properties of epoxy nanocomposites filled with hybrid MWCNTs/GNPs. Chapter Three presents on how the research was conducted, method chosen and the characterization used. The flowchart of overall research methodology from beginning until the end was also included in this chapter. Results and discussion obtained from the research are includes in chapter four. All the results and figures from the testing and characterization were placed and comprehensively discussed in this chapter. Lastly, the synopsis of this research was concluded in the Chapter Five. Entire discussion about the introduction until the results and discussion parts will be concluded in this chapter.

CHAPTER 2

LITERATURE REVIEW

2.1 Epoxy as matrix

In polymer, epoxy resin (EPs) have been widely applied as matrix resin in many fields due to their ease of curing and processing, good dimensional stability, superior electrical, chemical and mechanical properties (Mariappan *et al*., 2014; Zhou *et al*., 2015; Zotti *et al*., 2015). Besides, epoxy thermosetting resin can also be used to coat and cured the end products (Alaaddin *et al*., 2016). However, in polymer matrix composites, epoxies are commonly used as matrices to bind the reinforcements as well as to transfer load during their actual service (Michael *et al*., 2012). There are several types of epoxy in polymer such as bisphenol-A type which is commonly used epoxy, bisphenol-F type and novolac (Maureen *et al*., 2012). There are many other types of epoxy but, most are not suitable to a wide variety of applications. Besides, to convert epoxy resin to epoxy plastic, a reaction with suitable substance is required which is called hardener. The examples of epoxy hardener are amines, amides, acid anhydrides, imidazoles, boron trifluoride complexes, phenol, mercaptans and metal oxides (Remi *et al*., 2014; Gopal *et al*., 2017). In this research, the diglycidyl ether of bisphenol-A was used as matrices and mix with hardener that will disperse with MWCNTs/GNPs in order to improve their thermo-mechanical properties of basic epoxy resin system. Epoxy resins are compound that contains of more than one epoxide group and the commercial epoxy resins contained aliphatic, cycloaliphatic or aromatic backbones (Nagarjuna *et al*., 2014). The most important intermediate for epoxy resins is the diglycidyl ether of bisphenol that derived from a highly reactive compound of epichlorohydrin. The base chemical structure of epoxy resin is the three-membered ring which consisted of one oxygen atom and two carbon atoms as depicted in the following Figure 2.1 (Maureen, 2012).

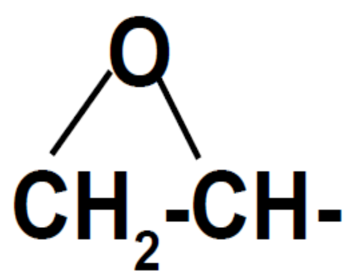

Figure 2.1: Base chemical structure of epoxy group (Maureen, 2012)

Phenolic glycidyl ethers are formed by the condensation reaction between epichlorohydrin and a phenol group. The structure of pure DGEBA shown in Figure 2.2 is the first commercial epoxy resin that are most widely used. DGEBA epoxy was used in this research because of their good properties in comparison with other thermosetting materials (Maureen, 2012).